PATENT SPECIFICATION (11) 1341557

1341557

(21) Application No. 26602/70 (22) Filed 2 June 1970

(23) Complete Specification filed 1 Sept. 1971

(44) Complete Specification published 28 Dec. 1973

(51) International Classification B01F 13/02 3/12 C11D 11/02// B01F 11/00

(52) Index at acceptance

B1C 14 19C1 21 30 4 5 6

C5D 6A4A 6A5B 6A5D2 6A5E 6A8B 6B1 6B10A 6B12B1 6B12E 6B12G2A 6B12G2B 6B12N1 6B2 6B7 6C6 6D

(72) Inventors PAUL BRANDT and KARL JOHAN SEVERIN JENSEN

(54) MANUFACTURE OF PULVERULENT COMPOSITIONS

(71) We, THE DANISH OIL MILLS AND SOAP FACTORIES LIMITED, a Danish Company of Oliemoellen, Copenhagen, Denmark and ANHYDRO AKTIESELSKABET, a Danish Company, of 8, Ostmarken, Soborg, Copenhagen, Denmark, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

This invention relates to the manufacture of pulverulent compositions which, though they contain a number of discrete materials, are homogeneous in the sense of being a uniform admixture of such materials. The invention is particularly, but not exclusively, applicable to the manufacture of blended pulverulent detergent compositions.

Blended pulverulent compositions have for many years been prepared by a process of spray drying in which solutions of the various ingredients are sprayed down a tower through which there is a current of warm air. The water from the solutions is evaporated by this air stream and a fine powdery solid collects at the base of the tower. This is mixed with other ingredients which are heat-sensitive or these may be fed into the lower portion of the spray drying tower. Such processes, though capable of high throughput, involve a high capital cost. Moreover, in the manufacture of detergent compositions by spray drying, it is difficult to control the degree of hydration of the sodium tripolyphosphate ingredient, which usually is the major component at present in compositions of this kind. In addition, spray drying can cause degradation of the sodium tripolyphosphate. It is also necessary to prepare any organic sulphonate or sulphate constituents in a pre-neutralised form and this involves preparing viscous slurries containing at least 40% of water which has to be removed during the spray drying operation.

It has been proposed in British Patent Specification No. 1,118,908 to produce blended detergent compositions in a turbulent air mixer wherein a previously formed mixture of individual pulverulent detergent components is sprayed with surface-active solutions or dispersions and/or with water, provided that the sodium tripolyphosphate which is so sprayed contains at least 20% by weight of phase I form thereof. The turbulent air mixer is a mixing device wherein during operation the individual solid particles are air-borne and form a cloud and it is into such a cloud that the liquids are sprayed. However, if an acceptable throughput is to be obtained with such a mixer, the residence time of the composition in the mixing zone usually has to be made such that it is too short for the hydration reaction of the sodium tripolyphosphate to have proceeded to an extent such that the product is non-stick. Therefore, in practice, an ageing period of storage is required before the detergent composition can be packaged for sale. Such period is usually about 24 hours. The short residence time also precludes the satisfactory *in situ* neutralisation of sulphonic acids unless, likewise, the finished composition is subsequently allowed to age. Moreover, in the aforesaid specification the various pulverulent components are fed into the spray mixing zone in a premixed state so that, in practice, two separate mixing operations are involved.

It has also been proposed (Detergent Age, April, 1967, 20—22) to spray solutions of organic sulphonic acid and of caustic soda on to a solid substrate composed of a heterogeneous mixture of pulverulent detergent ingredients which, after spraying, is agitated

by a series of rotating baffles to produce a homogentous laundry detergent composition. However the apparatus and method described do not provide for the high heat of neutralisation of the sulphonic acid to be dissipated readily and the same disadvantage would occur if a spray of water were used to hydrate sodium tripolyphosphate in the apparatus described.

According to the invention there is provided a method for the continuous manufacture of a blended pulverulent compositioned formed from both solid and liquid components, wherein a plurality of pulverulent components are fed heterogeneously into a mixing zone, in which they are maintained in the form of a fluid bed or particles by by means of the passage of a gas therethrough and in which they are mixed, the said fluid bed is sprayed by at least one liquid at or near the entry ponit of the pulverulent components to the mixing zone, and substantially homogeneous and agglomerated composition is continuously withdrawn from the mixing zone a differential gas pressure being maintained along the fluid bed in such a way as to produce a substantially uniform degree of fluidisation.

The invention also provides an apparatus for the manufacture of a blended pulverulent composition formed from both solid and liquid components, which apparatus comprises a mixing chamber adapted to contain a fluid bed of particles therein; ducting means to the said chamber for the passage during operation of a gas through the said fluid bed; a plurality of means for continuously feeding heterogeneously to said mixing chamber metered quantities of a plurality of pulverulent components; at least one nozzle for spraying the fluid bed with liquid at or near the entry point of the pulverulent components to the mixing chamber; means for continuously removing from the mixing chamber a substantially homogeneously blended and agglomerated pulverulent composition, and means for maintaining differential gas pressure along the fluid bed in such a way as to produce a substantially uniform degree of fluidisation.

By use of the invention pulverulent detergent compositions of a homogeneous nature can readily and continuously be prepared in simple apparatus of low capital cost but with high throughput. In use of the invention the fluidising gas stream serves to remove the heats of neutralisation of sulphonic acid and/or of hydration of sodium tripolyphosphate and the denser nature of the composition during mixing, as compared with the airborne particles in a turbulent air mixer, enables a greater throughput of material and/or the use of apparatus that is more compact. This method of mixing solid and liquid materials to form a homogeneous and agglomerated admixture can also find use in other technological areas.

By way only of example a preferred form of apparatus according to the invention will now be described with reference to Figure 1 and Figure 2 of the accompanying drawings.

Figure 1 shows such an apparatus partly in perspective and partly by way of a schematic representation, and Figure 2 shows part of our arrangement of such an apparatus in longitudinal section.

The apparatus shown in Figure 1 comprises a box like air chamber 1 having a large upper surface covered by a fine mesh screen 2 above which is a cover 3 leading to a flue 4. The air chamber 1 contains ducting means leading from one or more air fans 5 and is mounted on flexible arms 6. There is a vibrator motor 6a which causes the screen 2 to vibrate. At one lateral end of the vibrating screen 2 there is an inclined plane 7 serving to feed pulverulent material thereon to the screen surface, such material being fed to the inclined plane from a conveyor feed belt 8 above which are a number of hoppers 9 (three shown) each having a metering device 10. Alternatively, the feed belt 8 may be replaced by some other conveying means, for example by an enclosed vibrating tube. Above the inclined plane are a number of spray nozzles 11 through which different liquids may be sprayed from storage tanks 12 through line 13 and dosing pump 14, the atomisation of liquid being effected by air from a compressor unit 15 fed through connecting lines 16.

Thus a plurality of pulverulent materials may be fed in closely controlled quantities, but as a heterogeneous mixture, to the vibrating screen 2 above the air chamber 1 and this heterogeneous mixture is sprayed with one or more liquids from the nozzles 11 at the point of entry of the solids to the screen. The nozzles are each provided with a control valve (not shown). The vibration of the screen 2 causes the mixture of solds fed thereto from the inclined plane 7 to move across the screen and from the opposite lateral end of the screen 2 there is a chute 17 leading to a conveyor belt 18 which in turn leads to a hopper 19 and a bag or packet filling device 20 below the hopper. Thus the product emerging from the mixture zone is led directly to the bag-filling device 20.

During passage across the screen 2 the heterogeneous mixture of particles supported thereon is formed into a fluid bed by the passage of air through the screen from the fan 5 and air chamber 1 to the flue 4. The residence time of the solids in the fluid bed is arranged to be adequate for any reaction to be completed between one or more of the pulverulent materials and the liquids sprayed from the nozzles 11 and also for the pulveru-

lent materials to be thoroughly mixed so that a substantially homogeneous mixture is discharged down the chute 17. Heat from any such reaction is removed in the gas stream passing up the flue 4. This stream also contains the very fine particles which become airborne, the denser particles falling back on to the screen 2. The flue leads to a cyclone 21 where the solid particles are extracted and allowed to fall on to the inclined plane 7. Thus the fine particles are continuously recycled until they become agglomerated during the mixing process in the fluid bed and do not find their way into the discharged product. The discharged product can therefore be substantially dust-free. There is a further air fan 22 to extract the air from the cyclone 21. This air is discharged to the atmosphere through a flue 23.

To enable heat-sensitive and/or moisture-sensitive materials to be added to the fluid bed there is a further hopper 24 from which material therein may be discharged through a metering device 25 and a chute 26 directly on to the vibrating screen 2 at a point towards its discharge end.

In using the above-described apparatus in the method of the invention to produce a blended pulverulent detergent composition, pulverulent detergent ingredients are fed into the hoppers 9 from which accurately controlled amounts of each ingredient can be discharged on to the feed belt 8. Such hoppers will usually contain such ingredients as sodium tripolyphosphate, pre - neutralised organic sulphonate salt, soap and sodium silicate; sodium carbonate, sodium sulphate and/or sodium borate may also be added in this way, if desired. In addition to, or instead of, sodium tripolyphosphate other detergent builder salts can be employed. For example, sodium or potassium pyrophosphates, sodium trimetaphosphate, trisodium nitrilotriacetate, 1 - hydroxy - 1, 1 - ethylidenediphosphonic acid or amino - tris - methylenephosphonic acid may be used. The organic sulphonates are normally of two kinds: namely the C_{8-15} — alkyl benzenesulphonates used as surface-active agents and toluene-or xylene-sulphonates used as hydrotropes. Where it is desired that the final product should have a low bulk density it is preferred to employ some or all of the pulverulent components in a form having a low bulk density, such as that produced by spray drying. Although the method of the invention involves the heterogeneous feeding of a plurality of individual pulverulent components to a mixing zone, that is the mixture of solid components fed to the fluid bed has not been previously mixed to a homogeneous state, premixing will usually be carried out of components which are employed only in minor amount. For example in the preparation of detergent compositions colouring material, optical brightening agent, carboxymethylcellulose and sequestering agent, such as ethylenediamine-tetra-acetic acid, may often be conveniently pre-mixed with each other or with one of the other components.

The heterogeneous mixture of pulverulent components fed to the fluid bed is sprayed with one or more liquids which are also fed in metered quantities. In the preparation of detergent compositions such liquids may, and preferably do, include water for *in situ* hydration of sodium tripolyphosphate; organic sulphonic acids and/or fatty carboxylic acids, caustic soda solution for neutralisation of such sulphonic and/or carboylic acids; and/or liquid sodium silicate; and/or liquid or pasty detergent ingredients. The last mentioned may include non-ionic surfactants which are not readily obtained in pulverulent form, such as condensates of ethylene oxide with fatty acids, fatty alcohols or alkyl-substituted phenols as well as fatty acid alkyl-olamides. There may also be added in this way solutions of anionic surfactants such as sodium alkyl sulphates, sodium olefin sulphonates, sodium alkyl polyoxyethylene sulphates and sodium alkylbenzene sulphonates. For each liquid added the rate of addition can be closely controlled so that appropriate quantities can be incorporated in the final blended composition.

Any of the ingredients which may be incorporated as pulverulent solids may if desired, be added in the form of a solution spray. For example, perfume and/or sequestering agent may often be added to detergent compositions in this way.

Heat-sensitive and/or moisture-sensitive materials are preferably added to the mixing zone at a later point, that is towards the discharge end of the mixing zone. In the manufacture of detergent compositions there may be added in this way sodium perborate and/or other peroxy compounds; and/or active chlorine compounds, such as chlorinated sodium phosphate and chloroisocyanurates. Enzymes may also be incoporated in detergent compositions at such a point, for example by use of a further liquid spray on to the bed or by the addition of a conglomerate of the enzyme with a substrate, such as a condensed phosphate or hydrotrope. Alternatively the enzyme may be added as a solid or liquid at or near to the entrance of the mixing zone.

During the mixing process the particle size of the ingredients often increases. Particularly in a horizontal fluid bed of the type illustrated this leads to a particle size gradient across the screen 2. To ensure an even degree of fluidisation in the particle bed, therefore, means are provided for maintaining a differential air pressure along the bed in such a way as to produce a substantially

even degree of fluidisation despite the particle size difference.

Such a means is shown in Figure 2. Pulverulent material is supplied to the fluid bed as indicated by the arrow A, and air is supplied to the underside of the screen 2. The air chamber 1 is divided into three compartments 1a, 1b, and 1c by divider plates 30. Air is supplied to the compartments past dampers 31 which separately control the flow of air to the respective compartments. Using this apparatus the flow of air can be separately adjusted to each of the compartments in such a way as to give a substantially even degree of fluidisation along the bed.

An additional refinement which can be made to the apparatus is to provide air probes above the perforated plate for injecting air intermittently into the fluid bed. The main purpose of the probes is to help in maintaining flow of powder during the start up period of the apparatus until the correct fluid stabilisation has been achieved. The probes are simple air pipes each having a plurality of outlet holes (e.g. four) and a pressure gauge. When applied to the apparatus shown in Figure 2, one exemplary arrangement is to place one probe in the centre of the first section (i.e. the section fed by air from the first compartment (a), two probes in the centre of the third section, and one probe a short distance from the outlet. In a typical apparatus this short distance would be of the order of 10 cm. and each probe would be 2 cm. above the perforated screen 2.

If desired, the fluidising gas stream, which is usually an air stream, may be pre-heated to assist with the removal of excess moisture from the composition.

As an alternative to the machine illustrated, the invention may be worked in an apparatus with a vertical fluid bed having feed means to the top thereof for the various pulverulent particles, either as a single stream or as separate streams, and with continuous removal of part of the base of the fluid bed. In such a case the top of the bed will be sprayed with the liquid components and/or reactants and again any heat of reaction will be dissipated by the fluidising gas stream.

In the initial stages of the method according to the invention the emerging product may not be completely homogeneous, but such material can be readily recycled and it is usually found that the mixing system reaches a satisfactory equilibrium in under 0.5 hour. The residence time of the components in the mixing zone is preferably 10—15 minutes and it is found that such time is normally quite sufficient for the production of a substantially homogeneous product suitable for immediate packaging.

Whilst the invention has particularly been described with reference to the production of detergent compositions, it may be used to manufacture other blended pulverulent compositions which consist of an intimate admixture of individual components. For instance, food products such as instant milk powder, may be made in this way as also can granulated fertilizer compositions. Of course all such compositions must involve the admixture of a plurality of pulverulent solids with one or more liquids.

The invention is further illustrated by the following Example describing the production of a blended pulverulent detergent composition carried out in an apparatus as illustrated in the drawing. All quantities are given on the basis of the weights of components added during a given time interval.

Example

From six separate hoppers 9 there were metered on to the feed belt 8: (a) sodium tripolyphosphate (41.6 parts), (b) sodium silicate of density 0.08 g/cc (11.46 parts), (c) spray-dried soap (7.9 parts), (d) soda ash of density 0.55 g/cc (6.24 parts); (e) a condensate of cetyl/steryl alcohol with 50 mols of ethylene oxide (3.12 parts); and (f) a mixture of carboxymethylcellulose (2.257 part) and optical brightening agents (0.085 parts). From three separate spray nozzles 11 there were fed: (i) a mixture of a 30% solution of caustic soda (2.795 parts), a 40% solution of ethylenediaminetetra-acetic acid (0.065 part), sodium xylenesulphonate (0.265 part) and additional water (2.355 parts); (ii) dodecylbenzene sulphonic acid (6.73 parts); and (iii) perfume (0.121 part). Sodium perborate (15.02 parts) was metered in from the hopper 24 near to the discharge end of the screen 2. The air velocity through the bed was about 1m/sec. and particles which became airborne through the flue were recycled from the cyclone 21. The resulting product was entirely homogeneous and substantially dust-free. It had a bulk density of 0.3 g/cc and could be immediately packed for sale.

Comparative Example

As a comparison a composition of the same constitution was prepared on a spray mix apparatus as illustrated in British Patent Specification No. 1,118,908. The resulting product has a less desirable bulk density of 0.36 g/cc. Moreover this was sticky and not free-flowing to the same degree as that obtained from the above Example and it contained a significant proportion of fine dust particles.

WHAT WE CLAIM IS:

1. A method for the continuous manufacture of a blended pulverulent composition formed from both solid and liquid components, wherein a plurality of pulverulent

components are fed heterogeneously into a mixing zone, in which they are maintained in the form of a fluid bed of particles by means of the passage of a gas therethrough and in which they are mixed, the said fluid bed is sprayed by at least one liquid at or near the entry point of the pulverulent components to the mixing zone, and substantially homogeneous and agglomerated composition is continuously withdrawn from the mixing zone a differential gas pressure being maintained along the fluid bed in such a way as to produce a substantially uniform degree of fluidisation.

2. A method as claimed in claim 1, wherein at least one of the pulverulent components is itself a mixture of a plurality of inpredients.

3. A method as claimed in claim 1 or 2, wherein further materials which are heat-sensitive and/or moisture sensitive are added to the fluid bed at a point in the region of its discharge end.

4. A method as claimed in any preceding claim wherein a gas chamber, comprising a plurality of gas compartments is provided below a screen each supplying gas to a different region of the screen to maintain the fluid bed, the supply of gas to each compartment being separately adjustable.

5. A method as claimed in any preceding claim, wherein the said gas is preheated.

6. A method as claimed in any preceding claim, wherein the said gas is air.

7. A method as claimed in any preceding claim, wherein additional gas is introduced into the fluid bed from above to maintain flow of fluid bed material during start up of the apparatus.

8. A method as claimed in any preceding claim, wherein during the initial stages material withdrawn from the mixing zone to recycled for further mixing.

9. A method as claimed in any preceding claim, wherein the said pulverulent composition is a detergent composition.

10. A method as claimed in claim 9, wherein the composition includes sodium tripolyphosphate and the said at least one liquid comprises water for *in situ* hydration thereof.

11. A method for the continuous manufacture of a blended pulverulent composition substantially as herein described with reference to the accompanying drawings.

12. A method for the continuous manufacture of a blended pulverulent composition substantially as herein described with reference to the Examples.

13. A composition when produced by the method as claimed in any preceding claim.

14. An apparatus for the manufacture of a blended pulverulent composition formed from both solid and liquid components, which apparatus comprises a mixing chamber adapted to contain a fluid bed of particles therein; ducting means to the said chamber for the passage during operation of a gas through the said fluid bed; a plurality of means for continuously feeding heterogeneously to said mixing chamber metered quantities of a plurality of pulverulent components; at least one nozzle for spraying the fluid bed with liquid at or near the entry point of the pulverulent components to the mixing chamber; means for continuously removing from the mixing chamber a substantially homogeneously blended and agglomerated pulverulent composition, and means for maintaining differential gas pressure along the fluid bed in such a way as to produce a substantially uniform degree of fluidisation.

15. An apparatus as claimed in claim 14, wherein means are provided for adding further materials to the fluid bed at a point in the region of its discharge end.

16. An apparatus as claimed in claim 14 or 15, wherein the mixing chamber is defined at its lower side by a vibratable screen and the said ducting means pass to a gas chamber below the said screen.

17. An apparatus as claimed in any one of claims 14 to 16, wherein the gas chamber is divided into a plurality of compartments each of which communicates with a different region of the screen, the supply of gas to each compartment being separately adjustable.

18. An apparatus as claimed in any one of claims 14 to 17, wherein means are provided for introducing additional gas into the fluid bed from above to maintain flow of fluid bed material during start up of the apparatus.

19. An apparatus as claimed in claim 18, wherein the means for introducing additional gas comprise a plurality of pipes positioned above the screen, each pipe having a plurality of outlet holes.

20. An apparatus as claimed in any one of claims 14 to 19, wherein the fluid bed extends horizontally and material is introduced into and withdrawn from the fluid bed laterally.

21. An apparatus as claimed in any of claims 14 to 20, wherein the fluid bed is vertical and material is introduced at the top of the fluid bed and withdrawn from the bottom of the fluid bed.

22. An apparatus as claimed in any one of claims 14 to 21, which is arranged so that the said gas passes from the mixing chamber into a cyclone separator from where solids removed thereby are recycled to the mixing chamber.

23. An apparatus for the manufacture of a blended pulverulent composition substan-

tially as herein described with reference to the accompanying drawings.

24. A blended pulverulent composition whenever produced using an apparatus as claimed in any one of claims 14 to 23.

ELKINGTON AND FIFE,
Chartered Patent Agents,
High Holborn House,
52/54 High Holborn,
London, WC1V 6SH.
Agents for the Applicants.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1973.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

1,341,557 COMPLETE SPECIFICATION
2 SHEETS

This drawing is a reproduction of the Original on a reduced scale.
SHEET 1

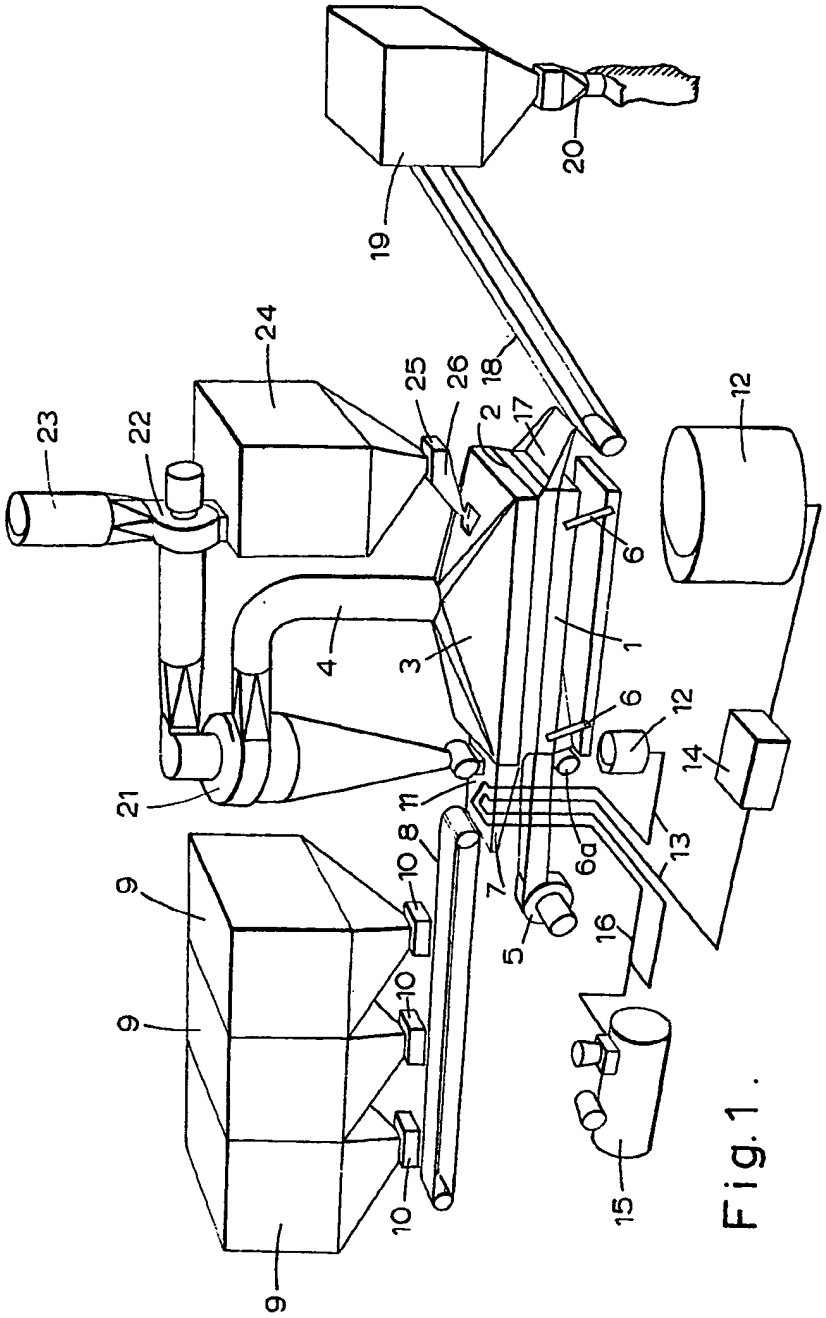

Fig. 1.

1,341,557 COMPLETE SPECIFICATION
2 SHEETS
This drawing is a reproduction of the Original on a reduced scale.
SHEET 2

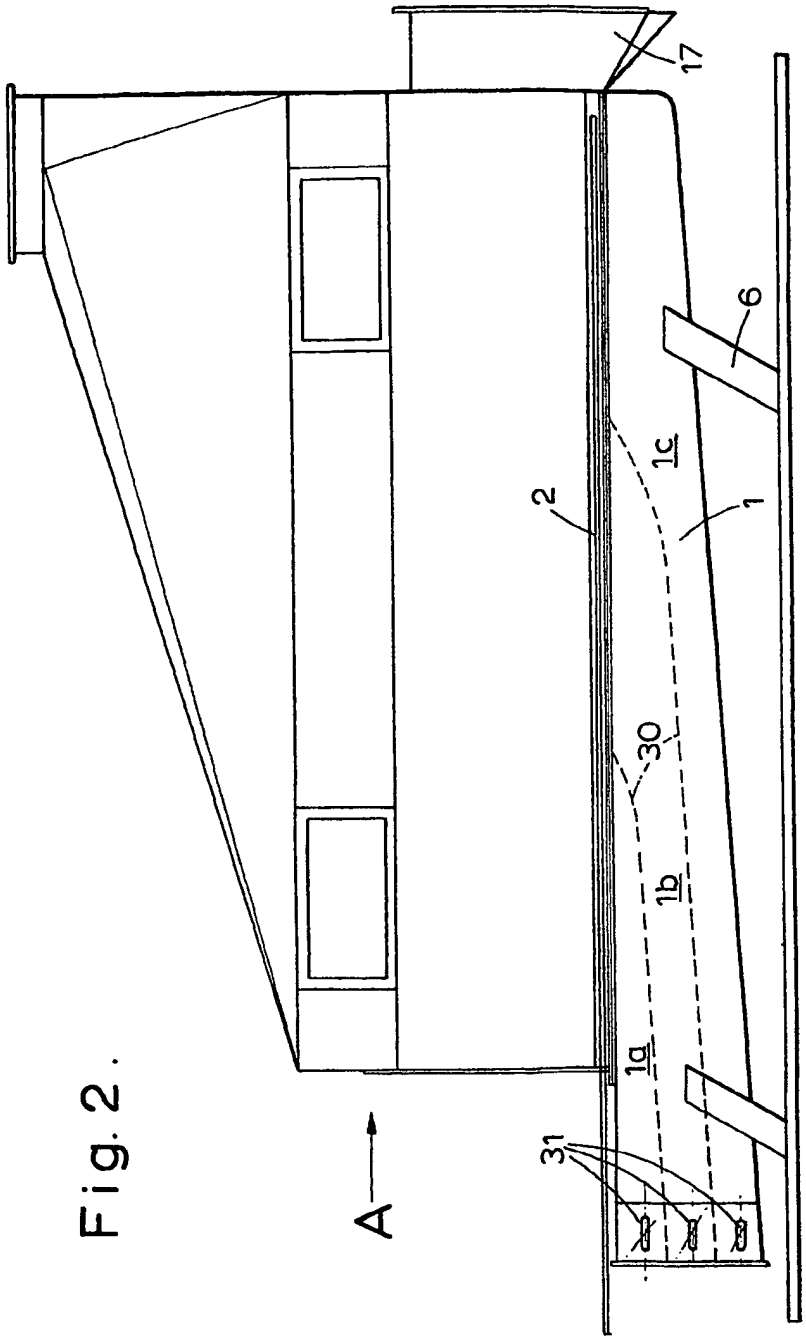

Fig. 2.